

# Features and Applications of Newly-Developed GC-TOFMS “The AccuTOF GC”

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## Introduction

A gas-chromatograph mass spectrometer (GC-MS) is a combined analyzer that has superior ability in analyzing organic compounds qualitatively and quantitatively. The first part, gas chromatograph, separates the compounds included in a sample (mixture), then the second part, mass spectrometer, obtains mass spectra of the compounds to carry out qualitative analysis. Quantitative analysis can be carried out as well from the peak area of the mass chromatogram of the compound.

As a mass spectrometer of a GC-MS system, several types of mass spectrometers are on the market, such as magnetic field, quadrupole (QMS), ion trap (ITD), and time-of-flight (TOF). Each mass spectrometer has its own features and applications.

By the way, “fast GC”, one of the GC methods, has become to attract attention recently. The fast GC method can shorten the analysis time remarkably while keeping a good separation ability equal to the conventional GC methods, by using a narrow and short column of about 0.1 mm inside diameter and 10 m long. The fast GC method, adopted in a GC-MS system, has the ability to improve the system throughput. However, it requires a fast spectrum-acquisition speed to the mass spectrometer, because the chromatograph peaks are narrower in time than a conventional GC. TOFMS only has the ability to satisfy the demand for fast spectrum-acquisition speed at the present time, but the existing GC-TOFMS systems are not satisfactory by either of the following reasons: it can follow the fast speed of the fast GC, but its mass resolution is too low to measure accurate mass, or, on the inverse, it has a mass resolution high enough to measure accurate masses but cannot follow the fast speed of the fast GC.

JEOL has developed and announced an innovative GC-TOFMS instrument, JMS-T100GC “The AccuTOF GC” in September of 2004, which satisfies both demands for high speed responding to the fast GC method, and for obtaining accurate mass easily.

The AccuTOF GC inherits the features of high resolution, accurate mass measurement with simple operation, and high sensitivity from its sister instrument, JMS-T100LC “The

AccuTOF.” The AccuTOF series contains a continuous averager in the data acquisition system that offers a wider dynamic range when compared to the time-to-digital converter (TDC) used in a conventional GC-TOFMS. In addition to this, the AccuTOF GC supports the fast GC/MS measurement, and is the first instrument that realizes these features in one instrument, which was impossible for the conventional instruments.

We have reported the principal features and the basic performances of the AccuTOF GC in the preceding 2003 MS Users Meeting. Here, we discuss the applications of the AccuTOF GC, in addition to the features and the basic performances.

## Overview

### Basic configuration

The basic configuration of the AccuTOF GC is as follows:

- TOFMS main unit  
(EI ion source is the standard)
- GC (Agilent 6890N)
- Personal computer
- Printer

Options include:

- Direct Injection Probe  
(Direct Exposure Probe (DEP))
- GC Automatic Sampler  
(injector + 100 sample trays)
- CI Ion Source
- FD/FI Ion Source
- EZChrom  
(software for quantitative analysis)

A plug-and-socket ion chamber is provided for both the standard EI ion source and the optional CI ion source, which allows cleaning of the easily contaminated ion chamber only, and makes replacing the filament easy.

An isolation valve is provided between the ion transfer system and the analyzer. Closing it keeps the analyzer in a high vacuum even during the following occasions: replacing the column and maintenance of the ion source, when a large quantity of solvent flows from the GC during measurement, and in emergency such as power failure.

The direct injection probe is a DEP type; the sample is initially dissolved in a solvent,

and is applied to the platinum filament of the probe using a syringe.

### External view

Figure 1 shows the external view of the AccuTOF GC. The AccuTOF GC is an on-floor type and has casters at the bottom to facilitate transport of the system.

(Note: In order to prevent damage to the turbomolecular pump, the system cannot be moved while in operation.)

The AccuTOF GC has integrated a turbomolecular pump and a rotary pump into the main unit, resulting in an effective footprint equal to or smaller than a typical bench-top system.

## Features of the Instrument

Figure 2 shows the diagram of the AccuTOF GC. It comprises depending on the functions:

- Ion source and ion transfer system
- Analyzer
- Detector
- Data acquisition system
- Data system (personal computer)

### Ion source and ion transfer system

Figure 3 shows a plan-view sectioned diagram of the ion source and ion transfer system. The role of this system is to ionize the sample introduced from the GC, and to transfer the ions to the analyzer at a low kinetic energy of about 30 eV.

The plug-and-socket ion chamber, shown at the top left of Fig. 3, has two gas inlets. One at the upper right in the photo is the gas inlet from the GC, and another one at the lower right is the gas inlet from the sample-heating device for the standard sample and others. The plug-in structure facilitates easy maintenance.

In a GC-MS system, a large quantity of helium gas, used as the GC carrier gas, is introduced to the ion source. The helium gas is ionized and transferred to the analyzer together with the sample. The helium gas, because of its overwhelming volume, causes a serious space-charge effect including charging-up of the surrounding parts. Because the AccuTOF GC is an orthogonal accelerating time-of-flight mass spectrometer (oa-TOF MS), the ions



Fig. 1 External view of the AccuTOF GC (Includes an optional automatic sampler).

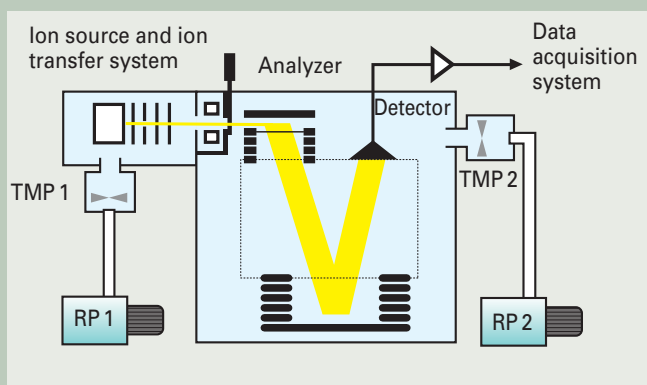


Fig. 2 Diagram of the AccuTOF GC.

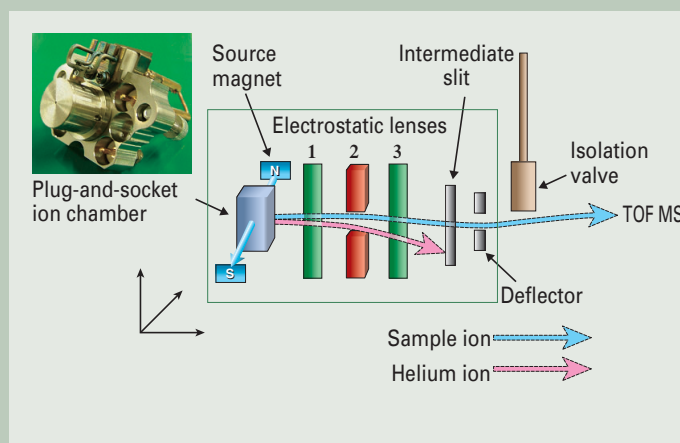


Fig. 3 Ion transfer system diagram.

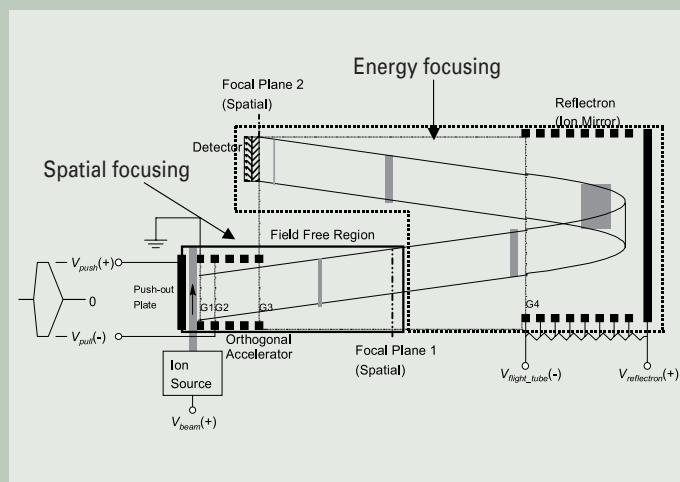


Fig. 4 Analyzer diagram.

must be transferred at a low kinetic energy of about 30 eV to the analyzer. Therefore, the ions are highly susceptible to the space-charge effect. Moreover, as all the ions, including helium ions, introduced to the analyzer reach the detector, the large quantity of helium ions might lead to a failure of the detector. To avoid the problem, the AccuTOF GC specifically developed an ion-transfer system that can remove more than 99% of helium ions before the ions enter the analyzer. The ion transfer system has the following three structural features:

- The electrostatic lens 2 is separated into two parts.
- An intermediate slit is installed.
- A deflector behind the intermediate slit.

In the EI ion source, a source magnet is placed to prevent dispersion of the electron beam emitted from the filament. By arranging the source magnet in a horizontal plane, an ionized ion accepts a force so that it is deflected downward, in case of a positive ion, while moving toward the analyzer. The extent of deflection differs according to the mass; the smaller the mass-to-charge ratio, the larger the deflection. The AccuTOF GC, making use of this mass selection ability of the source magnet, succeeded in colliding the helium ions with the plate of the intermediate slit and remove them, by optimizing the balance of the voltages of the upper and lower parts of the

electrostatic lens 2. The intermediate slit also assists the differential evacuation between the ion source and the analyzer. The ions passed through the intermediate slit are introduced to the analyzer with good efficiency due to the optimized deflector voltage.

In addition, the AccuTOF GC incorporates an isolation valve that isolates the ion transfer system from the analyzer. The isolation valve makes it possible to vent the ion source and carry out maintenance of it without venting the analyzer. Furthermore, it isolates the analyzer automatically in an emergency such as an unexpected stop of the evacuation system, which prevents the detector from degrading.

## Analyzer

The analyzer of the AccuTOF GC is an orthogonal accelerating time-of-flight mass spectrometer (oa-TOF MS) incorporating two-stage acceleration and a single-stage reflectron. It achieves high resolution owing to the spatial focusing by the two-stage acceleration and the energy focusing by the single-stage reflectron.

The diagram of analyzer of the AccuTOF GC is shown in Fig. 4. The sample is ionized in the ion source continuously, arranged in a parallel ion beam, and introduced to the space between the push-out plate and the grid 1 (G 1) in the orthogonal accelerator. To accelerate ions to the orthogonal direction, pulse volt-

ages,  $V_{push}$  and  $V_{pull}$ , are applied at the push-out plate and the grid 2 (G 2) respectively. A negative high voltage,  $V_{flight-tube}$ , is applied at the grid 3 (G 3) and the shield surrounding the field free region all the time, in case of analyzing positive ions. A positive voltage,  $V_{reflectron}$ , is always applied at the end of the reflectron.

## Detector

As we will see in the section “Data acquisition system,” when a time-to-digital converter (TDC) is used as the data acquisition system, the quality of a mass spectrum is hardly affected by the characteristics of the data acquisition system. But the TDC system is difficult to handle because it requires statistical correction of the acquired signal, and the mass accuracy depends on the accuracy of the parameter for the statistical correction. On the other hand, when a high-speed analog-to-digital converter (ADC) in combination with a continuous averager is used as the data acquisition system, the quality of a mass spectrum, such as mass resolution and peak shape, is directly affected by the characteristics of the data acquisition system, but this system has a merit that it does not require the statistical correction essentially. The AccuTOF GC adopts the ADC-with-continuous averager method, and a device to minimize the signal distortion

is installed.

The detector is mainly comprised of a micro channel plate (MCP) and an anode. The MCP is a glass plate approximately 0.6 mm thick having channels, that are honeycomb holes with an inside diameter of 10  $\mu\text{m}$  at intervals of 12  $\mu\text{m}$  (between channel centers). Both surfaces of the MCP are metal coated, serving as electrodes. A voltage applied between the electrodes will produce an electric-field gradient inside the channel.

When an electron hits the inner wall of the channel near the entrance, multiple secondary electrons will be emitted. These electrons will be accelerated by the electric-field gradient inside the channel, hitting the wall on the opposite side and emitting secondary electrons again. Thus, the electrons advance to the exit while hitting the inner wall of the channel repeatedly, resulting in a flow of electrons exponentially multiplied.

The electrons will be captured by the anode to produce an electrical signal. The amplification factor of the MCP (the number of electrons emitted from the exit when one ion is introduced to the entrance) is several thousands at maximum. Since TOF MS requires a detector having an amplification factor of  $10^6$ , it usually uses two MCPs layered (dual MCP).

## Data acquisition system

The data acquisition system digitizes electrical signals from the detector, arranges them into a format compatible with the data system,

and transfers them to the data system. The data acquisition system of an oa-TOF MS system must meet the following severe requirements.

### Acquiring data with extremely high time resolution

When the AccuTOF GC achieves a mass resolution of 5,000 (FWHM; full width at half maximum) with the molecular ion of octafluoronaphthalene ( $m/z$  272), the time of FWHM of the peak is 3 ns. To specify the peak position (= flight time = mass) as accurately as possible, it is said that at least 10 data points are necessary in the FWHM. Accordingly a time resolution of 300 ps is required for the data acquisition system of the AccuTOF GC.

### Acquiring data continuously

The system needs to begin acquiring data for the next ion flight as soon as one ion flight is completed. If there is a time lag between flights, the ion utilization ratio will decline because the ions that have passed through between the push-out plate and the grid 1 are wasted and not detected, resulting in poor sensitivity.

### Accumulating spectra in real time

The flight times of any ions will be shorter than 200 ms. When the  $m/z$  range to measure is less than 1,000, the flight time of ions will

be shorter than 55 ms. Therefore, when ion flights are repeated with this time intervals, ion flights of approximately 18,000 times per a second are counted. However, it is meaningless to try to get each flight data as an independent spectrum due to the following two reasons: First, each flight data is poor in S/N to be analyzed because the number of ions generated in the ion chamber in 1/18,000 second is small. Second, saving data of 18,000 spectra per second on a hard disk is utterly impractical in terms of data transfer speed and data capacity. Therefore, the data acquisition system acquires and accumulates multiple spectra for a specified period of time and forwards the accumulated data to the data system.

Two types of data acquisition systems meet these basic requirements, TDC and the ADC-with-continuous averager.

TDC (time-to-digital converter) is a kind of high-speed and high-accuracy stopwatch. It judges if any pulse of ions having a height exceeding a certain threshold level is detected or not in a specified measurement interval, resulting data of 1 (detected) or 0 (not detected). Even if multiple pulses are detected in one measurement interval, the later pulses are not counted, resulting in data of 1 (dead time loss). Thus, the TDC method requires a statistical correction, resulting in a low dynamic range as low as  $10^3$ , which is one of the demerits.

On the other hand, the ADC-with-continuous averager converts a signal from the amplifier with its high speed 8-bit analog-to-digital

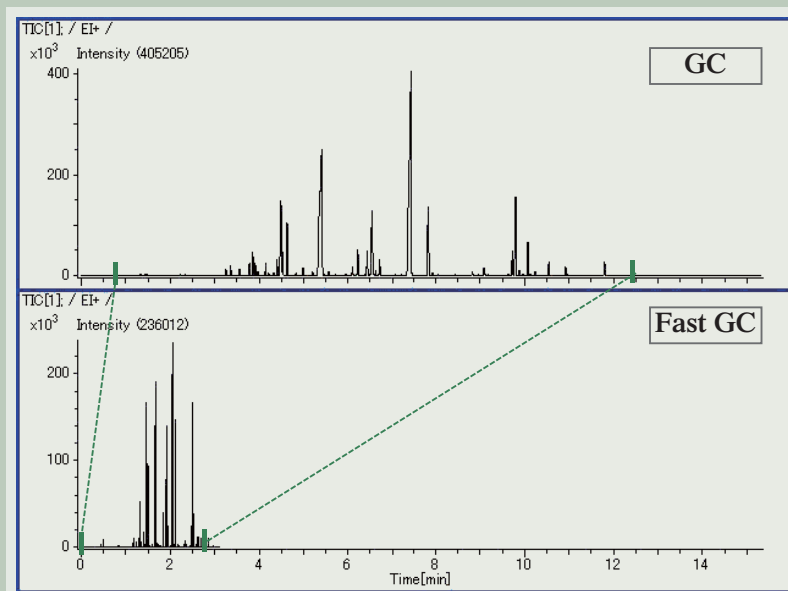


Fig. 5 Comparison of total ion chromatograms using conventional GC and fast GC methods (upper: conventional GC, lower: fast GC).

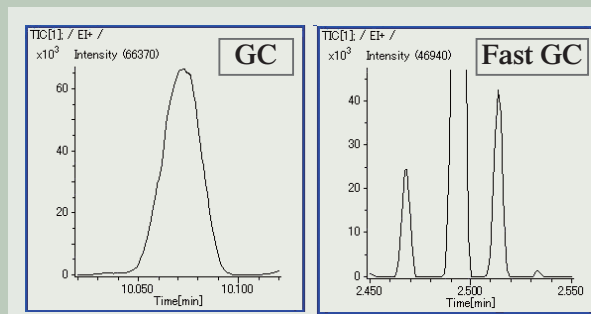


Fig. 6 Chromatogram peaks of  $\beta$ -farnesene measured using GC (left) and fast GC (right) methods (time range for both TIC is 0.1 minute).

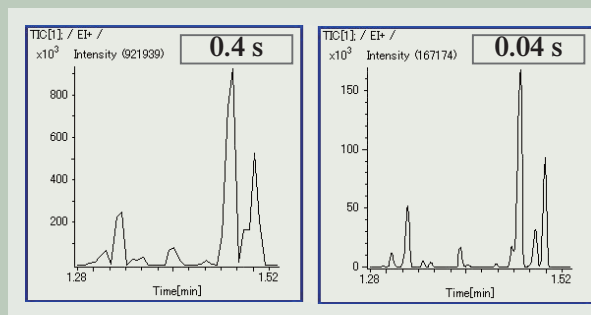


Fig. 7 Difference of chromatogram peaks with different spectrum-acquisition speeds (acquisition intervals) in fast GC method (left: 0.4 s, right: 0.04 s; both are data of AccuTOF GC).

converter (ADC) to a digital value of 0 to 255 (= 2<sup>8</sup>-1), and the data are accumulated in the summing memory. Therefore, the ADC-with-continuous averager basically does not need a statistical correction.

The AccuTOF GC adopts an ADC-with-continuous averager in the data acquisition system.

## Basic Performance

The basic performance of the AccuTOF GC is as follows.

- Resolution: 5,000 or more (FWHM, PFK m/z293)
- Mass range: 4 to 2,000
- Sensitivity
  - EI<sup>+</sup> mode: S/N ≥ 100, Octafluoronaphthalene, 1 pg (mass chromatogram of m/z 272, RMS)
  - CI<sup>+</sup> mode: S/N ≥ 150, Benzophenone, 100 pg (mass chromatogram of m/z 183, RMS)
  - Isobutane: 0.1 mL/min
  - CI<sup>-</sup> mode: S/N ≥ 20, Hexachlorobenzene, 100 fg (mass chromatogram of m/z 284, RMS)
  - Methane: 1.0 mL/min
- GC conditions:
  - Column: Agilent Technologies, DB-5ms 0.25 mm (inside diameter) × 30 m (length), 0.25 μm (film thickness)

Flow rate: Helium 1.0 mL/min (constant flow)

- Spectrum-acquisition speed: 0.04 s or longer (25 spectra/s or smaller)
- Mass accuracy: 2 mmu or 5 ppm (RMS, internal standard)

The AccuTOF GC has the features of high resolution, accurate mass measurement with easy operation, and high sensitivity as same as its sister instrument, JMS-T100LC "The AccuTOF." The AccuTOF GC furthermore attains a high spectrum-acquisition speed of 25 spectra per second, and fully corresponds to the fast GC/MS measurement.

We show data regarding the basic performance below, that are: fast GC/MS measurement, accurate mass measurement, stability, and dynamic range.

## Fast GC/MS measurement

As an example of the fast GC/MS measurement, an essential oil of lavender is measured. Here, we discuss the differences between the conventional GC and the fast GC methods, and the high spectrum-acquisition speed required for the fast GC/MS method. These two points are described briefly.

## What is fast GC method?

The fast GC method uses a narrow and short column, which shortens the analysis time while retaining a high-separation ability equiv-

alent to a conventional GC method.

An essential oil of lavender is measured using the AccuTOF GC with the conventional GC method, and also with the fast GC method, and the results are compared.

## GC parameters

- Sample injection: Split (1:500)
- Sample injection volume: 0.2 μL
- Oven program: 70°C (0.5 min) → <ramp rate: 10 °C/min> → 250°C (3 min)
- Column: DB-5ms, 0.25 mm (inside diameter) × 30 m (length), 0.25 μm (film thickness)

## Fast GC parameters

- Sample injection: Split (1:500)
- Sample injection volume: 0.2 μL
- Oven program: 70°C (0.5 min) → <ramp rate: 60°C/min> → 250 °C (3 min)
- Column: BPX-5, 0.1 mm (inside diameter) × 10 m (length), 0.1 μm (film thickness)

## MS parameters

- Mass measurement range: m/z 35 to 300
- Spectrum-acquisition speed: 0.04 s (25 spectra/s)

The parameters for GC and the fast GC differs in two points; column type and oven-temperature ramp rate. The fast GC uses a narrow and short column of 0.1 mm inside diameter and 10 m long, and the oven-temperature ramp

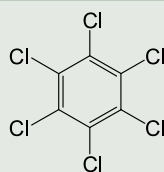


Fig. 8 Structural diagram of hexachlorobenzene (C<sub>6</sub>Cl<sub>6</sub>).

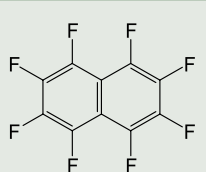


Fig. 10 Structural diagram of octafluoronaphthalene (C<sub>10</sub>F<sub>8</sub>).

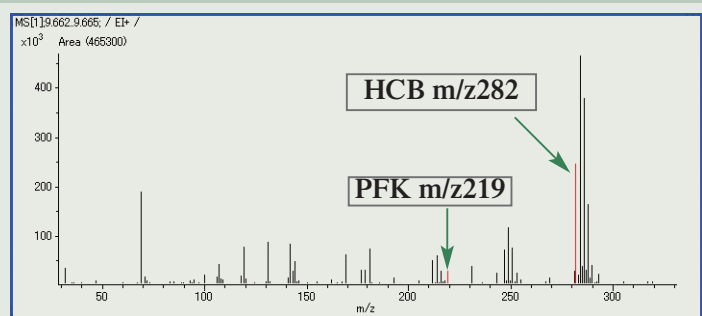


Fig. 9 Mass spectrum of mixture of PFK and hexachlorobenzene (2 ng).

Table 1 Measured masses of hexachlorobenzene with different concentrations are compared with the theoretical mass.

Sample concentration	Theoretical m/z	Measured m/z	Error (mmu)
3pg	281.81312	281.81233	- 0.79
10pg		281.81180	- 1.32
30pg		281.81196	- 1.16
100pg		281.81211	- 1.01
300pg		281.81160	- 1.52
1ng		281.81153	- 1.59
2ng		281.81214	- 0.98

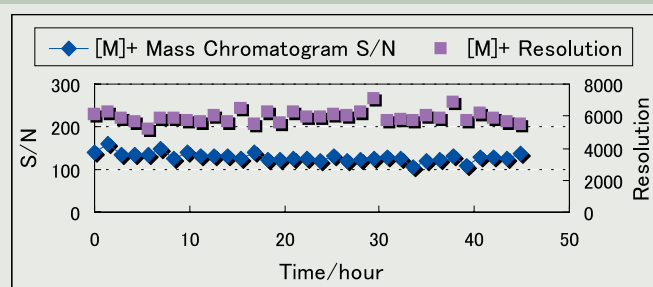


Fig. 11 Stability of sensitivity and resolution during the 45-hour continuous measurement. Sample: octafluoronaphthalene.

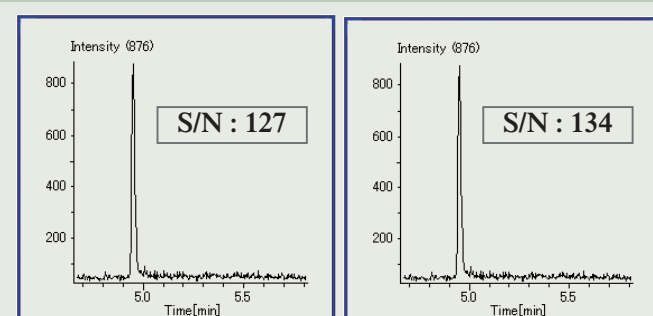


Fig. 12 Mass chromatograms of m/z 272 when starting (left) and 45 hours later (right).



rate is rapid as 60°C/min. If the rapid oven-temperature ramp rate of 60°C/min was applied to the conventional thick and long column, the peaks will overlap resulting in a poor resolution. To shorten the measurement time, it is necessary to raise the oven temperature rapidly and separate the sample rapidly. A narrow and short column satisfies this requirement.

The upper chromatogram in Fig. 5 shows a TIC taken using a conventional GC, which takes about 12 minutes, whereas, the lower chromatogram, using the fast GC, takes about 3 minutes, which is one fourth of the conventional GC. The throughput has improved four times concerning only the measurement time, excluding the preparation and data processing times. The fast GC method provides a high throughput GC/MS.

### Fast spectrum-acquisition speed required for fast GC/MS measurement

The fast GC method uses a narrow and short column. For that reason, chromatogram peaks in the fast GC/MS measurement are very sharp having widths of about 0.5 to 1 second, compared to 2 to 3 seconds using the conventional GC method (Fig. 6).

If a QMS, which is widely used in a GC-MS system, or a magnetic-field type MS, which is used for measurements such as dioxin to check for conformity with environmental regulations, is combined with a fast GC, it will not be able to acquire sufficient number of data points needed for each peak, because its spectrum-acquisition speed (scan speed) is 0.2 to 0.4 second. On the other hand, the AccuTOF GC can measure the total mass range in 0.04 second (25 spectra/s) and can follow the high-speed of the fast GC without losing the separation ability of the chromatograph and also, with high sensitivity.

Fig. 7 shows the results of the AccuTOF GC with different spectrum-acquisition speeds using the fast GC method.

The left chromatogram is measured with a spectrum-acquisition speed of 0.4 s, which is equal to the conventional magnetic-field MS and QMS, and the right is measured at a spectrum-acquisition speed of 0.04 s, the maximum speed of the AccuTOF GC. The difference between the two is quite obvious; for example at the retention time near 1.5 min, two sharp peaks are observed in the 0.04 s data, whereas the data of 0.4 s cannot separate the peaks because of the lack of data points.

As shown above, a fast spectrum-acquisition speed is necessary for the fast GC/MS measurement. The conventional magnetic-field and QMS mass spectrometers can not meet the high-speed requirement, but the AccuTOF GC can.

### Accurate mass measurement (one-point calibration)

The AccuTOF GC essentially has a high mass accuracy and therefore, calibration can be carried out correctly using the one-point calibration method. That is, the AccuTOF GC needs only one ion whose exact mass is known (internal standard ion) to measure accurate masses, whereas a magnetic-field mass spectrometer needs two or more internal standard

ions of known masses before and after the unknown peak. For example, hexachlorobenzene was analyzed as an unknown sample with PFK (m/z 219) as an internal standard for mass calibration (Fig. 9).

#### Sample

- Sample: Hexachlorobenzene (Fig. 8)
- Sample concentration: 3 pg/μL to 2 ng/μL (solvent: hexane)
- Internal standard for mass calibration: PFK

#### GC parameters

- Sample injection: Splitless
- Sample injection volume: 1.0 μL
- Oven program: 40°C (1 min) → <ramp rate: 20°C/min> → 280°C (3 min)
- Column: DB-5ms, 0.25 mm (inside diameter) × 30 m (length), 0.25 μm (film thickness)

#### MS parameters

- Mass measurement range: m/z 30 to 350

- Spectrum-acquisition speed: 0.2 s (5 spectra/s)

Table 1 shows measured masses of hexachlorobenzene with different concentrations. It shows such good mass accuracy that each mass error is smaller than -1.59 mmu.

Although we used m/z 219 of PFK in the measurement above as the mass calibration ion, m/z 207, 281 or others brought by column bleed when using a polydimethylsiloxane-bonded column can be used as the one-point calibration ion. That is, when an ion of known mass, originated in the column, is detected in the measured data, the ion can be used to calculate the accurate mass without using a standard sample.

#### Stability

Good stability when measuring continuously is one of the features of the AccuTOF GC. This comes from the stability of the newly-developed low-acceleration ion transfer system, in addition to the stability of the analyzer

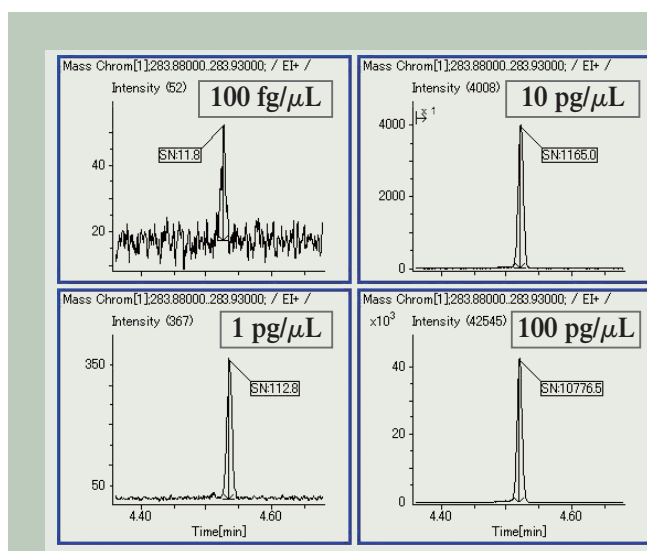


Fig. 13 Mass chromatograms of hexachlorobenzene (100 fg/μL, 1 pg/μL, 10 pg/μL, and 100 pg/μL).

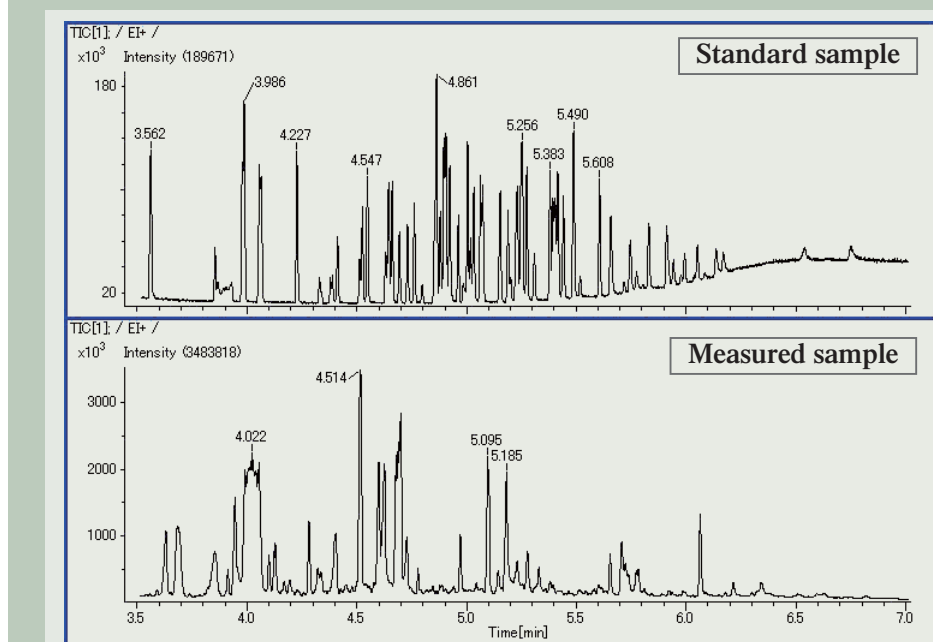


Fig. 14 Results of fast GC/MS measurements for standard sample (upper) and measured sample (lower).

already achieved by the AccuTOF. Stability is tested by measuring 1 pg of octafluoronaphthalene for 45 hours continuously (Fig.11). Octafluoronaphthalene is the sample used for specifying the sensitivity of EI positive mode.

### Sample

- Sample: Octafluoronaphthalene (Fig. 10)
- Sample concentration: 1 pg/ $\mu$ L (solvent: hexane)

### GC parameters

- Sample injection: Splitless
- Sample injection volume: 1.0  $\mu$ L
- Oven program: 40°C (1 min)  $\rightarrow$  <ramp rate: 20°C/min>  $\rightarrow$  280°C (3 min)
- Column: DB-5ms, 0.25 mm (inside diameter)  $\times$  30 m (length), 0.25  $\mu$ m (film thickness)

### MS parameters

- Mass measurement range: m/z 30 to 300
- Spectrum-acquisition speed: 0.2 s

(5 spectra/s)

At every measurement, the S/Ns of the chromatogram of m/z 272 were more than 100, and the mass resolutions at m/z 272 were more than 5,000. The sensitivity was very stable during the measurement time of 45 hours (approximately two days); the S/N was 127 at the start and 134 at 45 hours later (Fig. 12).

### Dynamic range

In order to demonstrate the dynamic range, hexachlorobenzene was analyzed at various concentrations ranging from 100 fg/ $\mu$ L to 100 pg/ $\mu$ L (100 fg/ $\mu$ L, 1 pg/ $\mu$ L, 10 pg/ $\mu$ L and 100 pg/ $\mu$ L) (Fig. 13).

The AccuTOF GC has a wider dynamic range than a conventional GC-TOFMS, realizing a dynamic range of  $10^3$  or more.

### Application Data

Here, we introduce the application data that demonstrate the features of the AccuTOF GC:

fast GC/MS measurement, improvement of selection ability using high-resolution mass chromatogram, and identifying unknown components by accurate mass measurement using CI method.

### Improvement of selection ability using high-resolution mass chromatogram

A magnetic field mass spectrometer can carry out quantitative and qualitative analysis with accuracy even when the sample contains many foreign materials (impurities), by taking advantage of its high-resolution analysis capability. In recent years, the high-resolution magnetic field mass spectrometers are playing an active part in the field of environmental analysis such as dioxin. Since the AccuTOF GC always operates at a high resolution with high sensitivity, it is expected to be applied to qualitative analysis of very small quantity compounds.

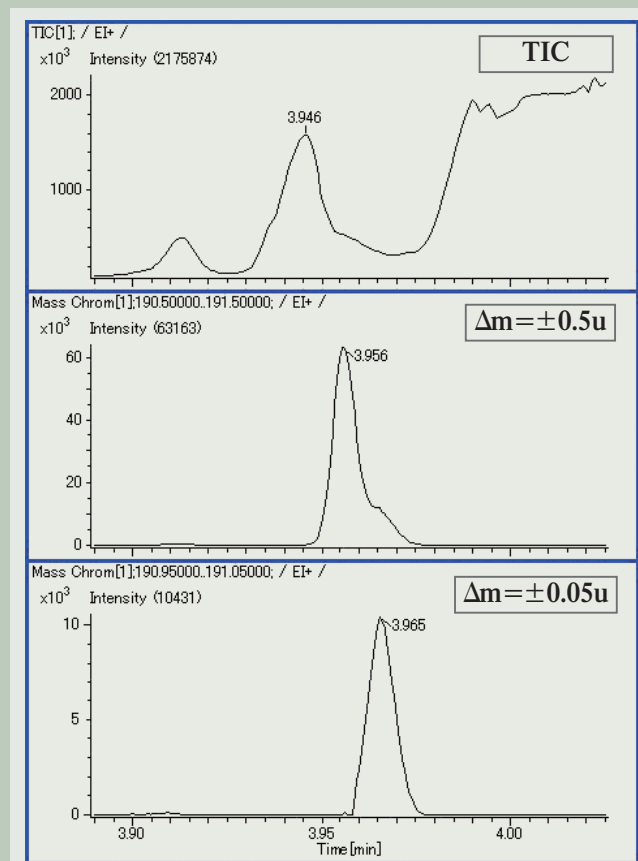


Fig. 15 TIC of the measured sample (top), and mass chromatograms of m/z 191 with  $\Delta m = \pm 0.5$  u (middle) and  $\pm 0.05$  u (bottom).

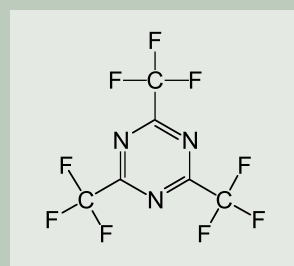


Fig. 16 Structural diagram of TTT ( $C_6N_3F_9$ ).

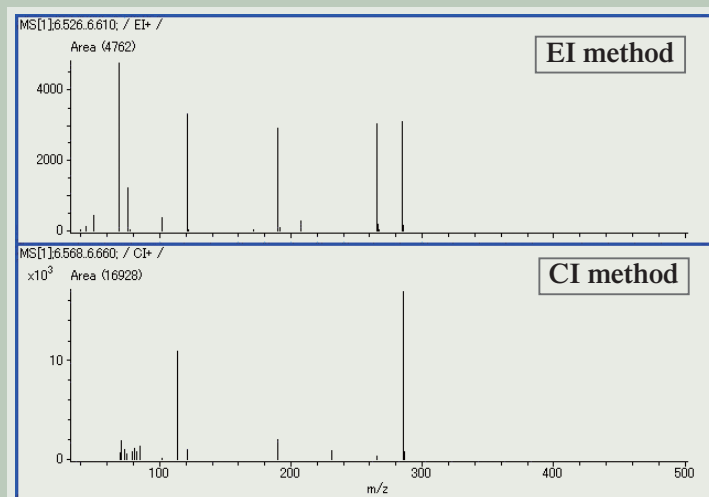


Fig. 17 Mass spectra of TTT (upper: EI method, lower: CI method).

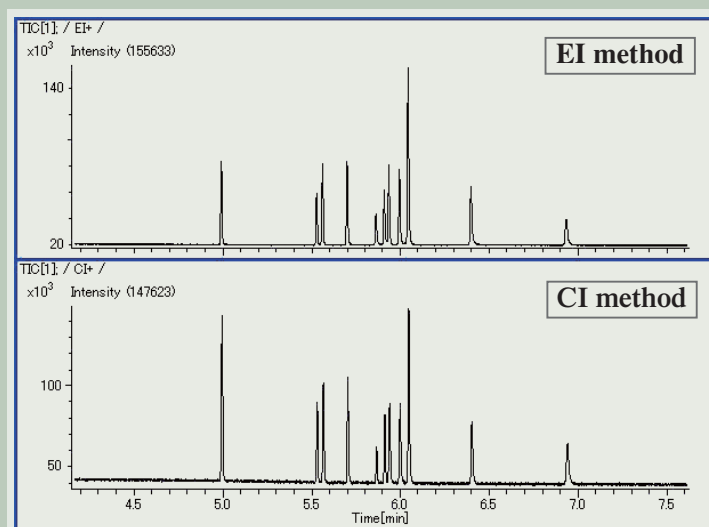


Fig. 18 TIC of liquid crystal (upper: EI method, lower: CI method).

In order to verify mass separation of a target compound from a sample containing many foreign materials using a high-resolution mass chromatogram, we added a standard sample, which includes 68 pesticides, into the extract from food, and verified that the compounds can be detected as a peak in a mass chromatogram. Measurement conditions and results are presented below.

### ■ Sample

- Standard sample: Includes 68 pesticides.
- Standard sample concentration: 50  $\mu\text{g}/\mu\text{L}$   
(solvent: hexane)
- Measured sample: Blank (extract from food) + standard sample

### ■ Fast GC parameters

- Sample injection: Splitless
- Sample injection volume: 1.0  $\mu\text{L}$
- Oven program: 40°C (1 min)  $\rightarrow$  <ramp rate: 50°C/min>  $\rightarrow$  300°C (1 min)
- Column: DB-5, 0.18 mm (inside diameter)  $\times$  10 m (length)  $\times$  0.18  $\mu\text{m}$  (film thickness)

### ■ MS parameters

- Mass measurement range:  $m/z$  30 to 500
- Spectrum-acquisition speed: 0.04 s  
(25 spectra/s)

Figure 14 shows the TICs of the standard sample (upper) and the measured sample (lower). The measured sample is prepared by spiking 50  $\mu\text{g}$  of standard sample into the blank (extract from food). The standard sample (upper) is clearly separated, and we could identify each pesticide even in the TIC. However, it is difficult to identify the standard sample in the TIC of the measured sample (lower), because the measured sample contains many foreign materials.

In the AccuTOF GC, when you create a mass chromatogram from measured data, a mass range (window width) must be specified. That is, if a wide mass range is specified, a low-resolution mass chromatogram equivalent to the conventional low-resolution measurement is obtained. On the other hand, if a narrow mass range is specified, a high-resolution mass chromatogram is obtained.

We examined what kind of mass chromatograms are obtained when we give two window width values,  $\Delta m = \pm 0.5$  u and  $\pm 0.05$  u, to the base peak of Chloroneb,  $[\text{M}-\text{CH}_3]^+$  ( $m/z$  191), which is one of the 68 pesticides (Fig. 15).

In the TIC (top), the intense background is observed, and the chromatogram is broad and dull. In the mass chromatogram with the window width  $\Delta m = \pm 0.5$  u (middle), a peak was observed at a retention time of 3.956 minutes. However, searching for this spectrum using the NIST library database identified that the compound is most possibly 2, 4-Di-tert-butylphenol, a different material from the spiked 68 pesticides. Next, in the mass chromatogram with the window width  $\Delta m = \pm 0.05$  u (bottom), a peak was observed at a retention time of 3.965 minutes. This peak was identified to be chloroneb using the NIST library database.

Thus, when we create a low-resolution mass chromatogram ( $\Delta m = \pm 0.5$  u, equivalent to QMS), it was difficult to find the compounds buried in the foreign materials; however, the high-resolution mass chromatogram ( $\Delta m = \pm 0.05$  u) enabled the identification of the com-

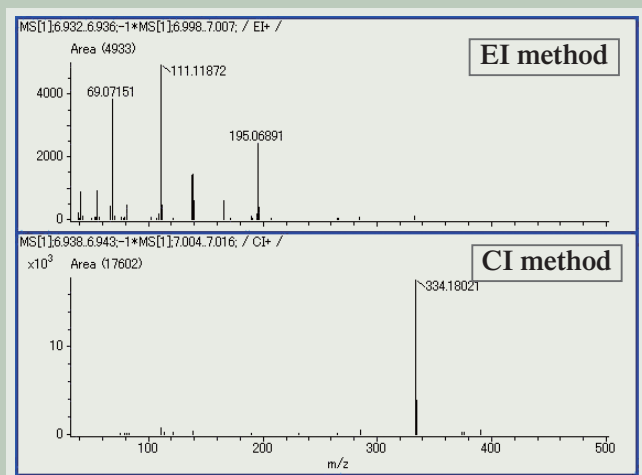


Fig. 19 Mass spectra of compound A (upper: EI method, lower: CI method).

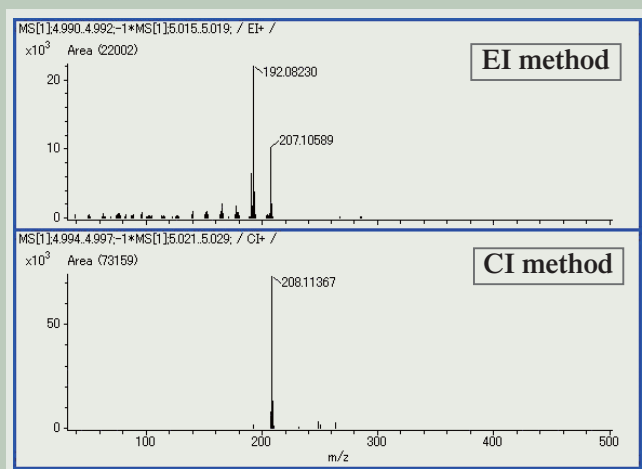


Fig. 20 Mass spectra of compound B (upper: EI method, lower: CI method).

Table 2 Calculated accurate mass of each ion.

Ionization method	Ion	Theoretical m/z	Measured m/z	Error (mmu)
EI method	$[\text{M}-\text{CH}_3]^+$	192.08132	192.08230	0.98
	$[\text{M}]^+$	207.10480	207.10589	1.09
CI method	$[\text{M}+\text{H}]^+$	208.11262	208.11367	1.05

Table 3 Composition estimation result of  $[\text{M}+\text{H}]^+$  in compound B.

Candidate	Measured m/z	Theoretical m/z	Error (mmu)	Estimated formula	Unsaturation number
No.1	334.18021	334.18070	-0.49	$\text{C}_{22}\text{H}_{24}\text{NO}_2$	11.5
No.2		334.18185	-1.64	$\text{C}_{19}\text{H}_{25}\text{FNO}_3$	7.5

Table 4 Estimated formula for each ion of compound B observed by EI method.

Ion	Measured m/z	Theoretical m/z	Error (mmu)	Estimated formula	Unsaturation number
$m/z$ 333	333.17432	333.17288	1.44	$\text{C}_{22}\text{H}_{23}\text{NO}_2$	12
$m/z$ 195	195.06891	195.06841	0.5	$\text{C}_{13}\text{H}_9\text{NO}$	10
$m/z$ 111	111.11872	111.11738	1.34	$\text{C}_8\text{H}_{15}$	1.5
$m/z$ 69	69.07042	69.07042	1.09	$\text{C}_6\text{H}_9$	1.5

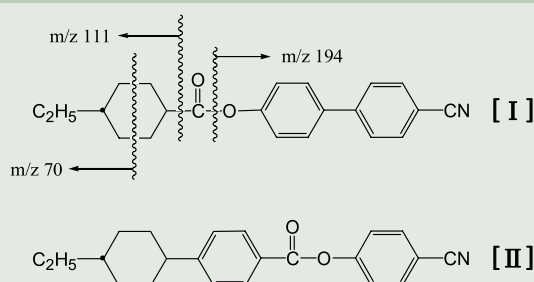


Fig. 21 Estimated structure of compound B.

pound.

In addition, we mention that the fast GC/MS measurement took only about six minutes to detect the 68 pesticides. It will take about thirty minutes for a conventional GC/MS measurement, demonstrating improvement of the throughput about five times.

### Identifying unknown compounds by accurate mass measurement using CI method

The process of the CI method is as follows: First, the reagent gas, for example, methane or isobutene, is introduced into a closed ionization chamber, and the reagent gas is ionized by the EI method. Next, the sample is introduced from the sample injection section (a GC or standard-sample injection section) into the ionization chamber. There, an ion-molecule reaction takes place between the reagent gas ions and the sample molecules resulting in the ionization of the sample.

The CI method is a soft ionization method compared to the EI method, and offers useful information for determining the molecular mass of unknown sample. As the reagent gas, methane, isobutene or ammonia is mainly used. Ions  $[M+H]^+$  are mainly observed when using the former two gases, and  $[M+NH_4]^+$  ions when using ammonia gas.

In the present experiment, we carried out a measurement that combines the CI method and "simple and accurate mass measurement", one of the features of the AccuTOF GC.

#### ■ Sample

- Sample: Liquid crystal in a commercially available pocket calculator was dissolved in a solvent (hexane).
- Internal standard compound: 2, 4, 6-Tris (trifluoromethyl)-1, 3, 5-triazine (abbreviated to TTT, Fig. 16)

#### ■ Fast GC parameters

- Sample injection: Split (1:400 (EI method), 1:200 (CI method))
- Sample injection volume: 1.0  $\mu$  L
- Oven program: 40°C (1 min)  $\rightarrow$  <ramp rate: 50°C/min>  $\rightarrow$  300°C (1 min)
- Column: DB-5, 0.18 mm (inside diameter)  $\times$  10 m (length)  $\times$  0.18  $\mu$  m (film thickness)

#### ■ MS parameters

- Measurement mass range: m/z 70 to 500
- Spectrum-acquisition speed: 0.04 s (25 spectra/s)

#### ■ CI parameters

- CI reagent gas: Isobutane
- Flow rate of CI reagent gas: 0.1 mL/min (controlled by mass-flow controller)

Figure 17 shows the mass spectra of TTT, the internal standard compound, obtained using EI (upper) and CI (lower) methods.

The TTT can be ionized by the CI method since it contains many nitrogen atoms, as well as by the EI method. Figure 17 indicates that  $[M]^+$  is obtained by the EI method and  $[M+H]^+$  by the CI method with good sensitivity. The accurate masses are calculated by one-point calibration using these ions. The measured data are shown below.

Figure 18 shows very sharp peaks since the injection method "split" is used in both EI and CI methods. To show an example of identification analysis, we selected the first peak A (compound A) at the retention time around 5.0 min and the last peak B (compound B) at the retention time around 7.0 min.

On the upper mass spectrum in Fig. 19, compound A by EI method, m/z 192 is observed as the base peak and the next intense peak is m/z 207. The lower mass spectrum in the figure, compound A by CI method, shows base peak of m/z 208. Therefore, it is inferred that m/z 207 ion observed using the EI method is the molecular ion of the compound A. The mass spectrum obtained by the EI method is searched for using the NIST library database, resulting in a compound with molecular mass of 207 as the first candidate (match: 912), that is, (1, 1'-Biphenyl)-4-carbonitrile, 4'-ethyl- ( $C_{15}H_{13}N$ ). As the next step, one-point calibration is carried out to calculate the accurate mass of it using TTT, the internal standard compound.

Accurate masses are calculated from the predicted structures of each ion (Table 2). As a result, measured values have mass errors of about 1 mmu from the theoretical values, showing very good accuracy. Thus, the compound A is determined to be (1, 1'-Biphenyl)-4-carbonitrile, 4'-ethyl- using the NIST library database search and the calculated accurate masses by using the EI and CI methods.

Next, the compound B is analyzed and discussed below. The obtained mass spectra are shown in Fig. 20.

On the upper mass spectrum in Fig. 20, compound B by EI method, m/z 111 is observed as the base peak, and m/z 69 and 195 as successive peaks. The lower mass spectrum in the figure (compound B by CI method) shows base peak of m/z 334. In the upper mass spectrum by EI, a small peak is observed at m/z 333. Therefore, it is inferred that m/z 333 is the molecular ion of the compound B. However, when we searched for the mass spectrum obtained by the EI method using the NIST library database, even the spectrum pattern of the first-candidate compound could not agree (match: 557). In addition, its molecular mass was not 333. Furthermore, other candidates did not have a molecular mass of 333. Thus, from the viewpoints of spectrum pattern and molecular mass, it is considered that there is a high possibility that this compound is not registered in the NIST library database. In order to find this unknown compound, we calculated accurate masses of each ion and estimated the composition.

Since the molecular mass of this compound is estimated to be 333, an odd number, it is considered, from the nitrogen rule, that the number of nitrogen atoms contained is odd. In the present study, estimation was carried out by aiming and estimating element species and their numbers, taking the representative liquid-crystal families into account [1]. Table 3 shows the result of the composition estimation by deducing from the accurate mass of m/z 334 in the mass spectrum obtained by the CI method. In estimating composition, the calculation was carried out with an error of 2 mmu or less.

When we consider the composition of candidate No. 2 from the compounds of the repre-

sentative liquid-crystal families, compounds having three oxygen atoms are narrowed down to azoxy compounds and p-cyano-phenyl-ester compounds of p-alkyl substitution benzoic acid. But, among these compounds, not one containing a fluorine atom has been reported [1]. From these facts, the composition of compound B is possibly and surely must be No. 1. We estimated the structure from the composition formula of No. 1 ( $C_{22}H_{24}NO_2$ ) and the fragment pattern obtained by the EI method. First, we estimated the composition formula from the accurate masses of the ions obtained by the EI method. Table 4 shows the results.

The candidate No. 1 contains one nitrogen atom, but it is known that there is no compound having an amino group (-NH<sub>2</sub>) or a nitro group (-NO<sub>2</sub>) in the liquid-crystal families. From this fact, it is estimated that the nitrogen atom in the candidate No. 1 exists in the form of a cyano group (-CN). The candidate No. 1 also includes two oxygen atoms and they are estimated to form an ester. In addition, since the unsaturation number of  $[M]^+$  is twelve, it is estimated that at least one or two benzene nuclei are included. As a result, two structures are deduced and shown in Fig. 21, that are p-cyanophenylester and cyclohexanecarboxylic acid aryl ester substitution product.

It is considered that m/z 111 is formed by a simple cleavage of an alkyl group, and m/z 69 is formed accompanying hydrogen transfer in a cyclohexane ring. These two ions can be generated from either structures [I] and [II]. However the ion m/z 195 is difficult to create from structure [II], and is deduced to arise from a simple cleavage of an alkoxy group accompanying hydrogen transfer in structure [I]. As a conclusion, the structure of the compound B is suggested to be structure [I] from the fragment ions obtained by the EI method.

## Conclusion

In the present paper, we introduced the features of the AccuTOF GC and its applications, including fast GC/MS measurement, accurate mass measurement, and improvement of selection ability using high-resolution mass chromatogram. In particular, it was demonstrated that measuring accurate masses using the EI and CI methods allows structural and qualitative analysis of the target compound with high reliability.

JMS-T100GC, the AccuTOF GC, is an innovative GC-MS that succeeds in obtaining the features that were impossible to attain simultaneously using conventional instruments. The features are: fast spectrum-acquisition speed that deals the fast GC/MS data, accurate mass measurement with simple operation, and stable, high sensitivity.

We hope the AccuTOF GC will help you in your research and studies.

## References

- [1] Liquid Crystal Compound Glossary, ed. Japan Society for the Promotion of Science, Baifukan Co., Ltd, Tokyo (in Japanese)